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COMPATIBILITY TESTING OF PRIMARY
EXPLOSIVES AND PYROTECHNICS

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SUMMARY

This report consists of the text of a paper given at the
Second Symposium on Chemical Problems connected with the
Stability of Explosives, Sweden. A general account is
given of the main factors involved in the compatibility
testing of primary explosives and pyrotechnics, and test
procedures are described for examining their compatibility
with materials used either in contact or close proximity.
Some results are discussed, particularly with reference to
the behaviour of lead azide.

CONTENTS

SUMMARY

Many ingredients of pyrotechnics and primary explosives are fairly reactive compounds and as such are susceptible to chemical incompatibility with the other materials with which they have to be used. Examples include lead azide, and the more reactive oxidants and metal powders used in pyrotechnics. Many of the reactions leading to incompatibility require the presence of water and procedures for testing for incompatibility must take this into account.

The need for compatibility testing applies not only to materials and explosives which are used in actual contact, but also to materials used in assemblies where no impermeable barrier exists to protect the explosive from vapour contamination. Primary explosives and, in some instances, pyrotechnics are particularly likely to be affected because of the small amounts which are used often in proximity to much larger quantities of other materials from which reactive vapours and water may be evolved during storage.

Test procedures for examining the compatibility of materials and explosives used either in contact or near each other are described and some results discussed, particularly with reference to the behaviour of lead azide.

Introduction

The increasing complexity of modern weapons, and the
large numbers of synthetic materials now available to weapon
designers, have caused increasing attention to be paid to the
avoidance of incompatibility between components. So far as
explosives are concerned, this is usually done by assessing
their chemical and thermal stability and by determining
whether these are adversely affected by the materials to be
used. The requirements in regard to compatibility are not easy
to satisfy, since weapons are normally stored for long periods
before they are put into use and allowance must usually be
made for the effects of severely adverse environments and bad
treatment.

Some idea of the scope of this work may be gained by
reference to the diagram of a hypothetical guided weapon shown
in figure 1. In such a weapon the warhead might be filled with
a charge based on one or more high explosives, and several
initiating compounds and pyrotechnics would be used to fill
detonators in the safety and arming unit and various auxiliary
units. The rocket motor with its igniter and propellant
fillings would provide further opportunities for incompatibilities
to arise between components.

As well as the obvious need for compatibility between
explosives and items with which they are in actual contact,
adverse effects may also arise between separated components due
to vapour interactions. In addition to considering the effects
of incompatibility on explosives, it is almost equally important
to determine whether the explosives themselves are likely to
affect structural components in their vicinity - as occurs for
example when corrosion of metal parts is observed or when
soluble explosive ingredients are absorbed.

This paper is restricted to the behaviour of pyrotechnics
and primary explosives which present certain characteristic
problems. The group includes the most sensitive or explosive
compositions of which practical use can be made and it is self-
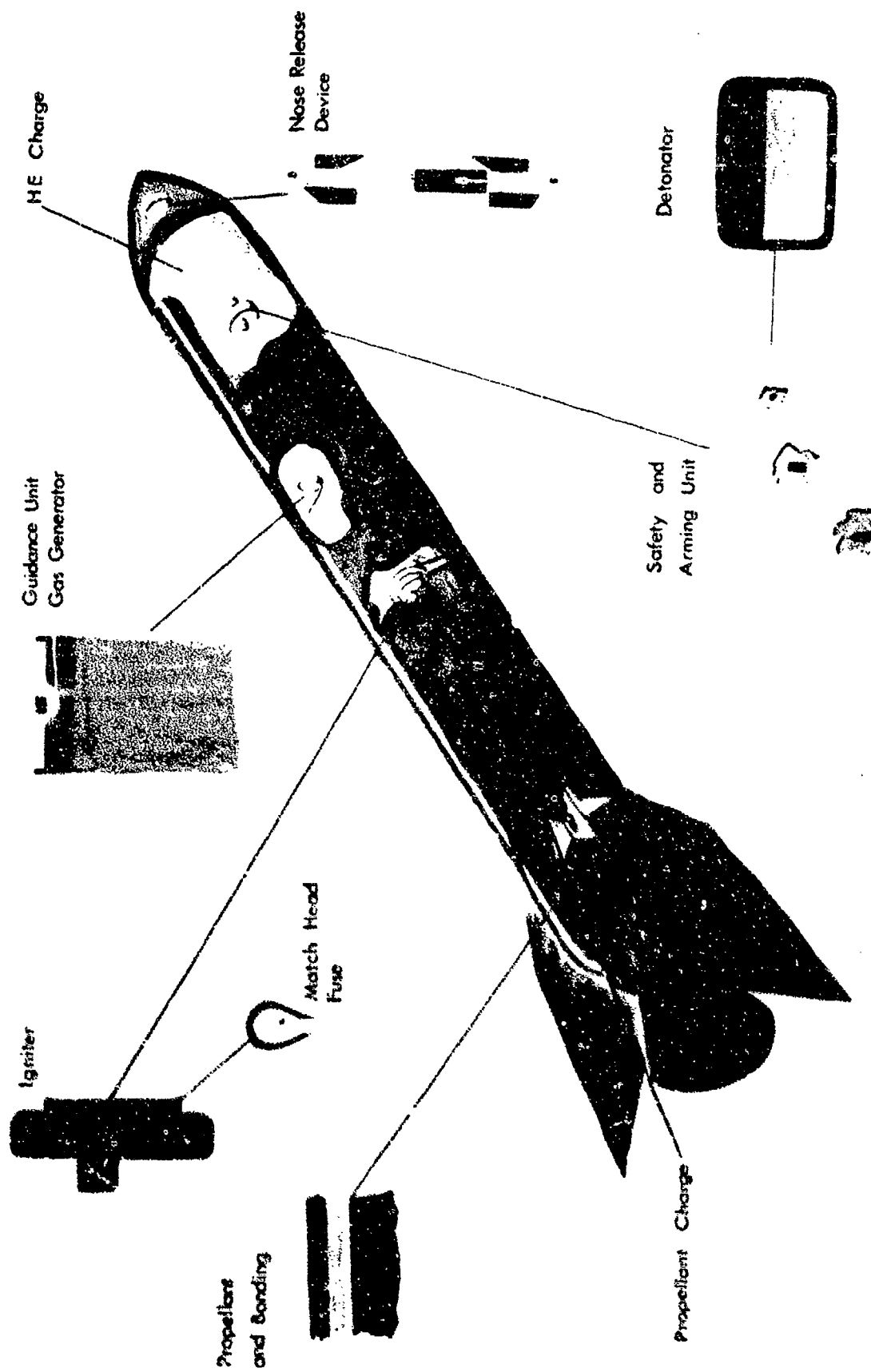
Figure 1. Diagram of a hypothetical guided weapon

Labels within figure:

HE Charge

Nose Release Device

Detonator

Guidance Unit Gas Generator

Safety and Arming Unit

Match Head Fuse

Igniter

Propellant and Bonding

Propellant Charge

-evident that the ease with which they are detonated by mild, relatively low-energy stimuli (friction, impact, electrostatic discharge, etc.) must not be further increased by contamination or by an ill-advised choice of ingredient or structural material. Potential reasons for increased hazard include: accidental contamination with gritty substances, formation of highly sensitive corrosion products and generation of high electrostatic charges on materials such as synthetic polymers. Although this paper is more concerned with chemical compatibility questions the importance of assessing the physical properties of candidate materials in regard to these hazards must be emphasized.

In any assessment of compatibility the circumstances of use and the design of the weapon largely define the compatibility requirement. However, almost invariably, the assessment does not relate to one round of ammunition or to a single operation, but to many hundreds of rounds or processes repeated many times. Attention must therefore be given to the consequences of abnormal occurences and the possibility of accidents and, in this particular regard, the physical properties of materials and their possible effects on sensitiveness are of the greatest importance.

Factors Influencing Compatibility

Thermal Stability: Most of the commonly used primary explosives and pyrotechnics possess adequate thermal stability for general purposes. Indeed, in many cases they are superior to propellants and high explosives in this respect and routine batch testing for chemical stability is not required. This has an important bearing on compatibility test procedures since there are no standardized stability test procedures which can be adapted for compatibility tests in the way that for example the vacuum stability test is frequently used for high explosives.

It is questionable whether a thermal stability test is an appropriate method for testing compatibility with an explosive whose thermal decomposition temperature (e.g. lead azide 250 ^{o}C) may be considerably higher than that of many of the nonexplosive

materials with which it is used. The thermal decomposition reactions of these explosives are not, as a rule, autocatalytic and the size of the explosive charges is frequently quite small. Therefore no concern usually arises about self-heating leading to spontaneous ignition as in the case, for example, nitroglycerine based propellants. Although tests at very high temperatures which reveal abnormal rates of gas or heat evolution may give relevant information they may simply record the reactivity of the breakdown products of the test material with the explosive under conditions which would never obtain in practice.

Chemical Reactivity: With such a considerable number of compounds under discussion it is impossible to generalize except to say that they are all chemically reactive and that deterioration by chemical attack is more likely than by thermal degradation. Also as a rule, these reactions will be more rapid under moist conditions and may not occur at all in the absence of moisture.

It is often more appropriate to check compatibility in the presence of moisture at relatively low temperatures rather than at high temperatures in conditions where moisture will be expelled during the early part of the test and play no further part in any reaction.

Effects of Charge Size: Primary explosives, and sometimes pyrotechnics as well, are used in small increments which may weigh only a few hundredths of a gram. These are placed in an assembly containing much larger quantities of other substances and, if not protected by effective sealing, may be exposed to the volatile compounds which many non-metallic materials are known to evolve.

It is evident that if 0.01 % of a reactive gaseous product is evolved by a component weighing 50 grams, this will amount to 5 milligrams which, if allowed to react with a charge of explosive weighing perhaps only 50 to 100 milligrams, could have quite serious effects. Tests in which equal amounts of explosive and material are mixed together and examined by a gas evolution or other test are not likely to be very relevant to this type of problem.

Properties_of Compatible_Materials: After what has already
been said, a number of desirable properties for compatible
materials can be listed as in table 1.

Table 1. Desirable properties for compatible materials

    Chemically non-reactive and stable
    Low water content, not hygroscopic
    Neutral reaction
    Low volatility and absence of volatile impurities
    Absence of soluble components
    No tendency to absorb soluble substances
    No tendency to acquire electrostatic charge
    Causes no friction or other mechanical hazard
    Specified composition, adequately controlled

Of course, there are few substances which would fulfil all
these requirements but the consideration of these properties in
particular candidate materials should influence the tests which
are applied.

The last requirement is of considerable practical importance,
since in many cases commercial products are involved and testing of
samples will be hardly worthwhile if the nature of the product
changes at a later date. In most circumstances the chemical composition
of commercial products is a secondary consideration being of minor
importance provided that physical properties are properly maintained.
In contrast, compatibility with explosives requires a degree of
chemical control which is rarely needed in normal circumstances in
non-military uses. In some cases, good control of physical properties
is of assistance, since this will hardly be obtained without resonably
good chemical control, but in general there are frequent difficulties
in specifying and maintaining supplies of compatible materials.

Type_of Application of_Candidate_Material: From what has
already been said it will be evident that any compatibility
assessment must be relevant to the use which is to be made of the
materials and explosives involved.

Table 2 lists some typical compatibility problems and the
questions which may have to be investigated.

Table 2. Some typical compatibility problems

Subject	Questions
1. Ingredients, either explosive or non-explosive, mixed to prepare a new composition	(a) Chemical reactivity between ingredients (b) Thermal stability of mixture (c) Sensitiveness properties of mixture
2. Explosive compositions used as adjacent fillings	(a) Chemical reactivity between ingredients and effects on thermal stability (b) Sensitiveness hazards
3. Metals used in contact with explosives	(a) Susceptibility to corrosion (b) Catalytic effects on explosive decomposition (c) Properties (sensitiveness) of corrosion products (d) Position in electrochemical series relative to metal salts in explosive
4. Metals used remotely	(a) Susceptibility to corrosion (b) Properties (including sensitiveness) of corrosion products
5. Non-metallic materials in contact with explosive	(a) Effect on thermal stability (b) Chemical reaction (c) Acidity/alkalinity (d) Moisture content and other volatiles (e) Interchange of soluble ingredients (f) Deterioration in contact with explosive (g) Methods of quality control (h) Electrical and mechanical properties and effects on sensitiveness hazards
6. Non-metallic materials used remotely	(a) Moisture content and other volatiles (b) Reactivity with vapours from explosive (c) Electrical properties

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All investigations should start with a general appraisal
on the above lines after which the techniques and test methods
to be applied can be decided. As has already been mentioned
most primary explosives and pyrotechnics are not subject to
spontaneous autocatalysed decompositions and therefore any
incompatibility is usually the result of a direct chemical
reaction. They are mostly crystalline solids and under dry
conditions do not react readily with other solids.
Incompatibility can frequently be traced to volatile impurities
or breakdown products from the material in question and some
consideration of the nature of these substances is therefore
appropriate.

This aspect of the behaviour of natural and synthetic
materials has received surprisingly limited attention until
recently, but is now becoming increasingly important in other
areas such as space exploration and submarines where men have
to live for long periods in a closed environment. Also the
performance of electronic equipment is subject to interference
since the resistance of contacts or insulation can be affected.
Investigation of the nature of volatiles has become easier in
the recent years due to advances in infrared and mass spectrometry
and gas chromatography, and the combination of the two latter
techniques. Gas sampling from a closed container above the test
material will frequently give sufficient material for analysis
after fairly short periods of storage.

Table 3 lists some common types of polymer and the volatile
compounds which they have been found to evolve at normal
temperatures. Not all specimens or types of the listed polymers
evolve all the listed volatiles but it is usual to find about
ten identifiable components. The sources of many of the volatiles
are fairly obvious, e.g. residual solvents, unreacted ingredients,
low molecular weight polymer fractions. Some are more obscure,
but the reasons for their occurence are of less importance to us
than the fact that many polymeric materials exhibit this
characteristic behaviour and that investigations of its effect
on explosives compatibility are often necessary.

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Table 3. Some common types of polymer and the volatile compounds evolved by them at normal temperature

	Polyurethane	Nylon	Epoxy Resins	ABS Resins	Silicone Rubber	Butyl Rubber	Natural Rubber
Carbon Monoxide	X	X	X	X	X	X	X
Carbon Dioxide	X					X	X
Methane	X	X	X	X	X	X	X
C_4 Unsaturated hydrocarbons					X		
Isobutylene						X	
Di and Tri-isobutylenes						X	
Benzene					X		
Toluene		X	X	X	X	X	X
Xylenes			X	X	X	X	X
Methanol	X				X		
Ethanol	X	X	X		X		
n-Propanol				X			
iso-Propanol					X		
n-Butanol	X	X			X		
sec "		X	X				
tert "					X		
2-Phenyl-2-propanol	X				X		
Acetone	X	X	X		X		X
2-Methyl-4-pentanone			X		X		
C_4-C_6 Hydrocarbons			X				
Ethylene			X				
Trichlorethylene				X			
Styrene				X			
Methyl Styrene				X			
Silicone Oils					X		
Acetophenone	X				X		
C_1-C_3 Alkyl benzenes	X						
1,3-Dioxane		X					
N-Methyl Morpholine		X					
2-Butanone			X				
Acetic Acid					X		
Ammonia				X			
Ethylamine				X			

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Pyrotechnics

The ingredients of pyrotechnics are, in most cases, substances which are individually, chemically stable and non-explosives, but which are chosen so as to react together with appropriate vigour when a necessary stimulus is applied. Essential to all compositions are a fuel and an oxidant or source of oxygen. Other ingredients are added to impart desired properties in performance, manufacture and filling, storage stability or other feature.

The stability of such mixtures is usually very good provided that reactions between ingredients, not necessarily those occurring during combustion, can be avoided and the mixture is protected from outside contamination particularly water.

Powdered metals such as magnesium, aluminium and zinc are frequently used as fuels in pyrotechnics in conjunction with metal salts such as nitrates and perchlorates as oxidants. Almost invariably the presence of excessive amounts of water in such mixture leads to corrosion of the metals, with deterioration in performance, evolution of gases with increase in pressure in sealed containers and, in the worst cases, danger of spontaneous ignition. It is usual for magnesium powder, which is the most rapidly attacked of the commonly used ingredients, to be coated with a suitable oil or resin as protection against moisture. This greatly improves its resistance to attack, but does not offer complete protection for prolonged storage in an excessively moist environment.

All materials which form part of the environment of pyrotechnics in service involving storage over long periods, whether they are in actual contact with the explosive or not, require careful scrutiny to confirm that the amount of water which they contain is within a tolerable limit. Most substances will absorb a certain amount of water, depending upon the temperature and relative humidity of their environment and if the temperature is raised or the humidity is lowered, will

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lose water by evaporation to achieve equilibrium under the new
conditions. Pyrotechnics, capable of reacting with water will
act as desiccants and since the reactions in many cases, e.g. of
metal powders, with water are irreversible they will tend to
continue until all available water is used up or until the metal
becomes so corroded as to be unreactive. Materials which normally
retain water quite tenaciously may yield it up under these
circumstances. Any rise in temperature will greatly favour the
process, increasing both the ease of release of water from its
source and the reactivity of the pyrotechnic.

The severity of the effects will depend upon the relative
amounts of the substances involved. Slight and normally tolerable
effects produced on a large pyrotechnic charge by a small component,
made from a material containing some water, may become very severe
in a store where the same substances are present but in reversed
proportions.

Consideration of the actual quantities of materials which
it is proposed to use is therefore important. It is normal practice
to use quite small quantities of explosive for some purposes, or
to design charges with a small surface area which has to be ignited.
If these explosive components are used in proximity to relatively
much larger amounts of other explosive or non explosive material,
particular care must be taken to ensure that they can tolerate
the environment in which they may have to stay for several years.
Vapours from plastics, rubbers, adhesives or other explosives, the
effects of which are normally insignificant, can produce serious
deterioration. The presence of strong and reactive oxidants e.g.
chromates and dichromates, lead peroxide, in some compositions
makes them particularly susceptible to deterioration caused by
oxidizable organic vapours such as are evolved by many plastics
and rubbers and some propellants.

Incompatibility resulting from direct contact between a
pyrotechnic and materials such as rubbers and plastics under
dry conditions is rather rare. Materials such as epoxy resins
which are frequently incompatible with other explosives are

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compatible in this sense with the common types of pyrotechnics. Account must be taken of the possibility of increased sensitiveness resulting from the use of the material, e.g. because of its gritty nature or the presence of sulphur, if the explosive contains a chlorate, but moisture is usually required to stimulate most chemical interactions.

Primary Explosives

There are of course many primary explosives and it is not possible to make many general comments which apply to all of them. However, one property which they all share is extreme sensitiveness, no increase in which can usually be tolerated, and secondly they are invariably used in very small amounts. Their chemical reactivity and stability varies widely and this of course has a considerable effect on their susceptibility to chemical incompatibility. Some, such as lead and barium styphnates and the lead dinitroresorcinates rarely prove to be incompatible with materials with which they are brought into contact, others such as lead azide are more reactive but even so the storage life of nearly all primary explosives would be almost infinite if they could be protected from chemical reactions with other substances. The importance of protective sealing of detonators in this connection has already been mentioned but recent trends in weapon design have tended to increase the possibility of compatibility difficulties with more varied and novel materials sealed hermetically into the same environment as the detonator by improved packaging techniques.

Most primary explosives are well defined crystalline substances whose chemical reactions often depend upon the presence of a certain amount of moisture. The effects of water are therefore important considerations in compatibility and stability assessments and the maintenance of a low humidity is beneficial to the good behaviour of these explosives during storage. It is however extremely difficult to reduce humidity

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below certain levels since most non metallic materials contain
some water which can be released in a dry atmosphere.

Test Methods

As has already been indicated, the choice of test method
depends upon the type of application which is involved. In the
following sections some of the more frequently used methods
and their scope are discussed.

Weight Loss Tests: Mixtures of pyrotechnic and test material
are heated in a small tube with a restricted neck so that
completely free access of air or escape of volatiles is hindered.
The test temperature is usually 100 $^\circ$C and the heating may
continue for 6 days with daily checks on weight losses. A
substantial loss in weight beyond that experienced by the
explosive and test material when heated separately, is cause
for concern but this type of test can be criticized on several
grounds which will be evident from what has already been said.
Volatiles and water tend to be expelled during the test, the
high temperature may produce effects which would never occur
in practice, and the absence of a weight change is not conclusive
evidence that no chemical change has occurred. The test can be
improved if it is followed by chemical examination of the
explosive, for decomposition products, for example for chlorides
from chlorate containing compositions.

Thermogravimetric analysis is a useful refinement of tests
relying on weight loss. Heating programmes including periods of
isothermal heating can be used and automatic programmers are
available for this. This is particularly useful for stability
assessment of primary explosives where the small sample size
which can be used is advantageous.

Differential Thermal Analysis: Much valuable information on
the decomposition of explosives has been obtained by DTA and
Differential Scanning Calorimetry. We have investigated the use
of DSC for compatibility testing particularly in respect to
propellants, but although incompatible materials can be

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detected by this means, these are always rather bad cases and the method is not as discriminating as the older test methods. This is unfortunate since the small sample size which is required is a very desirable feature so far as initiator work is concerned but it is perhaps too much to hope that a test lasting only a few minutes will give information relevant to months or years of storage. Sometimes however DSC has proved extremely useful particularly when problems concerned with high temperature behaviour are concerned.

The records shown in figure 2 are of tests on a solder flux which was proposed for use in sealing an assembly containing PDX. Contact with the flux lowered the temperature of the composition exotherm by several degrees and since the proposed operating temperature was close to this lowered decomposition point an obvious hazard would have existed.

Metal Corrosion Tests: From time to time as new metals are proposed for manufacture of, for example, detonator components or as new explosive compositions appear, checks have to be made of the likely severity of corrosion effects. This is done by storing small quantities of the explosive, under moist conditions, on test pieces of the metal usually at 50 or 60 ^{o}C and making a visual assessment of the results. With many compositions e.g. those containing chlorates or nitrates it is common to find some corrosive effect and this is then further investigated to find the threshold of humidity and temperature at which it is likely to become unacceptable. This judgement tends to be made after comparison with known systems.

The nature of corrosion products merits some attention since, once produced, these will contaminate the explosive. This is normally investigated by chemical and x-ray methods. The classic example is copper azide corrosion and a qualitative test based upon this reaction has been used in the UK for a number of years. This is shown in figure 3 and consists of suspending a strip of clean copper over a mixture of test
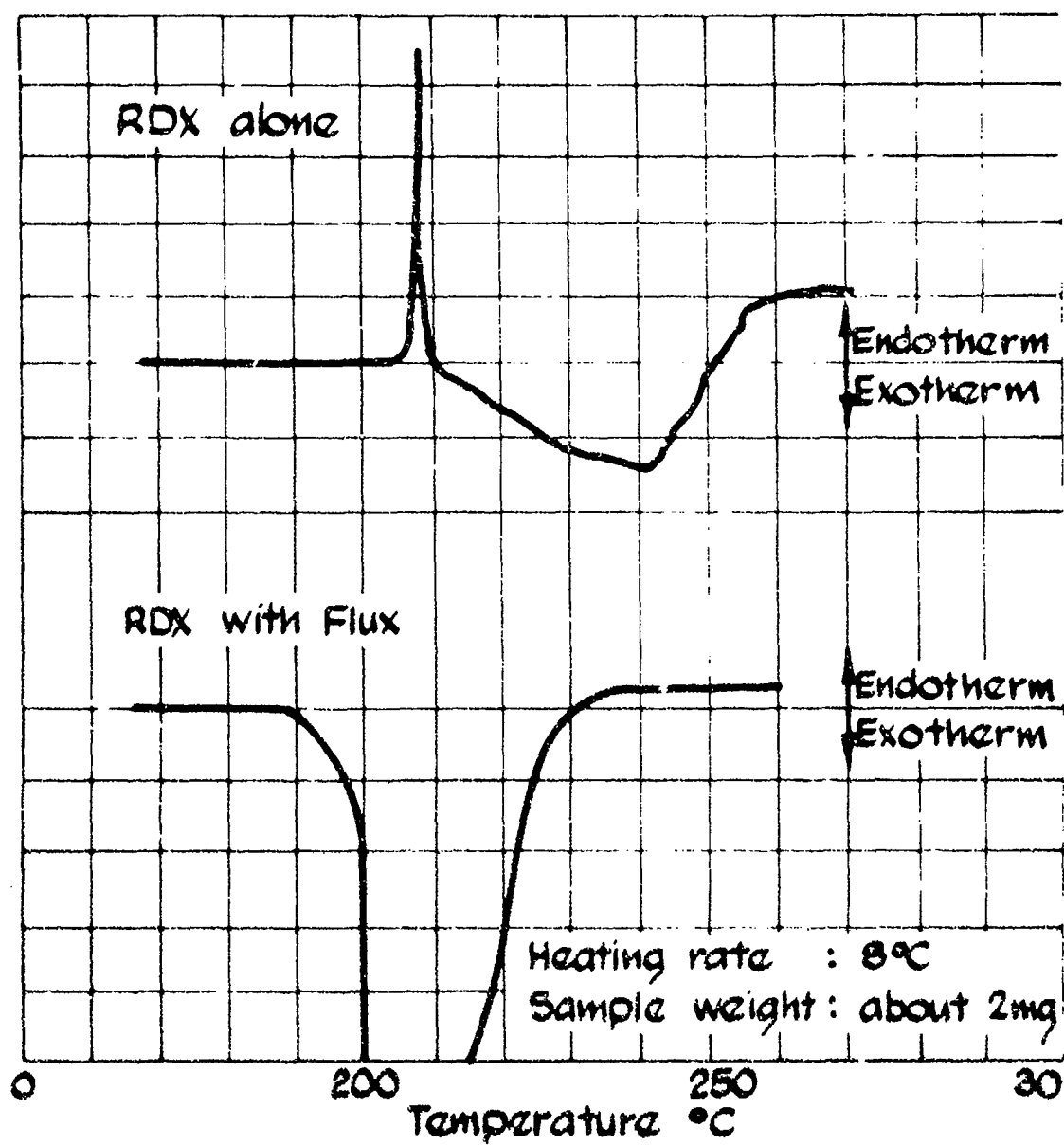
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Figure 2. DSC records of RDX alone and of RDX in contact with a solder flux

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material and moistened lead azide. Unsuitable materials
accelerate the decomposition of the azide and a greater
than normal degree of copper azide corrosion is observed.
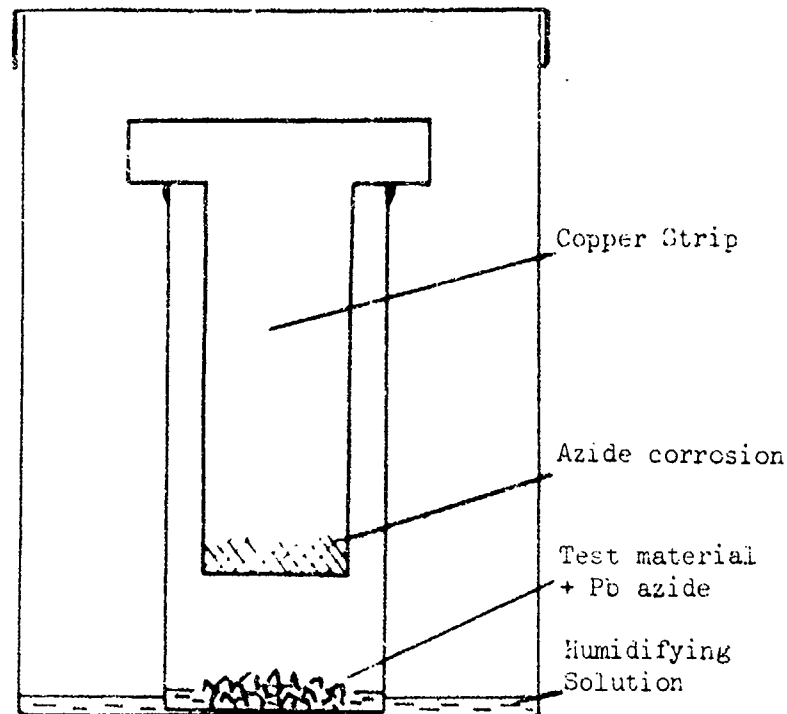

Figure 3. Copper strip test with lead azide

Gas Evolution Tests: A useful application of a gas
evolution test has been in testing materials to be used with
pyrotechnic materials containing metal powders such as
magnesium. Vacuum stability tests at moderate temperature
(60 and 80 ^{o}C) can measure the rates of hydrogen evolution
produced by reaction of water from the test material with
the metal powder and assist in judgement of whether the
effect is at a tolerably slow level.

Proximity Tests: These tests investigate the effects caused
on small explosive charges by exposing them to large quantities

of other materials. This can be done in various ways, varying the temperature, humidity, relative amounts of explosive and test material, the areas of their exposed surfaces, and size and shape of the reaction vessel. All these factors are liable to affect the results which are obtained and it is desirable to standardize the tests as far as possible.

A suitable test assembly is illustrated in figure 4 and is simply a small desiccator in which a small explosive sample is surrounded by a much larger quantity of test material. Humidifying solutions may be placed in the base of the desiccator. After exposure, the explosive is analysed chemically or by x-ray or other methods to assess the extent of deterioration. Most of the available results concern lead azide, although this type of test can be applied to any explosive and could be extended to detonators and igniters to test the adequacy of their sealing.
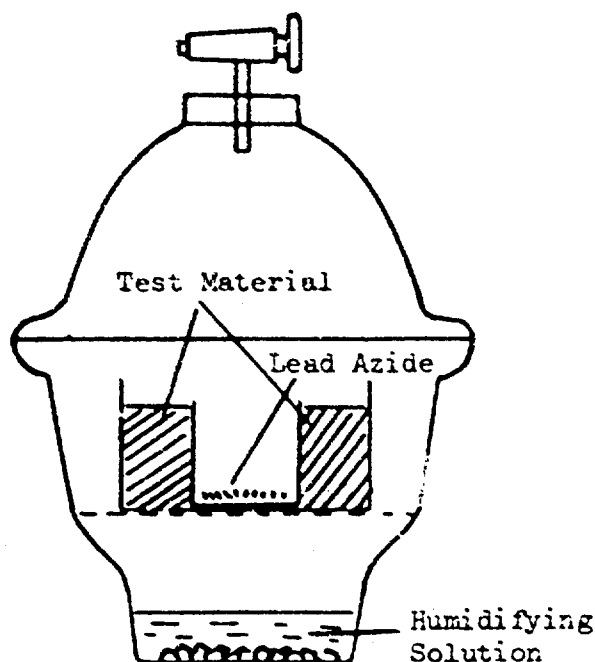


Figure 4. Initiator exposure trials

Lead Azide

Thermal Stability and Hydrolysis: Lead azide is
particularly susceptible to the effects described above. In
comparison to many other explosives, it possesses a very high
degree of thermal stability, and withstands long periods of
heating under vacuum conditions at temperatures as high as
175 $^{\circ}$C without appreciable decomposition. Any deterioration
occurring during ambient storage temperatures, in the absence
of visible or other radiation, will therefore in general be
caused by chemical reaction with a contaminating substance.

Lead azide is well known to be susceptible to hydrolysis,
and since it is usually impossible to ensure the complete
absence of water from its environment, hydrolysis is the most
important mode of decomposition to be considered when assessing
the compatiblility of other materials.

The hydrolysis equilibria of lead azide have been studied
by Fleitknecht and Sahli[1], and by Lamnevik, and papers dealing
with it were presented by Lamnevik, Todd and Blay at the
Symposium held at ERDE in October 1966[2].

The equation for the hydrolysis of lead azide in the
presence of water is given by Fleitknecht and Sahli as;

$$Pb(N_3)_2 \ (s) + H_2O \ (l) \rightleftharpoons Pb(OH)N_3 \ (s) + HN_3 \ (g) \qquad (i)$$
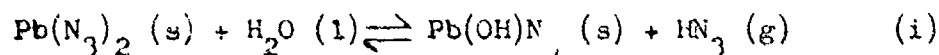
The equilibrium constant of the overall reaction is equal
to the partial pressure of hydrazoic acid vapour HN_3, and has
been calculated by Lamnevik as being 4.5×10^{-2} mm Hg at 25 $^{\circ}$C,
and 1.4×10^{-2} mm Hg at 20 $^{\circ}$C. Lamnevik also obtained some
experimental evidence that these values were not greatly in
error.

It appears therefore that lead azide, existing in a closed
system with water at ordinary temperatures, will hydrolyze to
produce only a very low partial pressure of hydrazoic acid.
Provided that the quantity of azide is not disproportionately
small in comparison to the volume of its container, and that
other influences do not alter the equilibrium, the extent of

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any deterioration should not be excessive. For example lead azide at equilibrium with water at 25 ^{o}C, in a container having a gas volume of 1 litre, should produce 0.12 mg of hydrazoic acid vapour, equivalent to about 0.4 mg of lead azide, and to this should be added the hydrazoic acid dissolved in any liquid water which is present, but this is not likely to be a considerable quantity in a normal environment.

Experiments in which lead azide is kept under hot moist conditions in the absence of factors which seriously disturb equilibrium, confirm that moisture alone does not necessarily have a very substantial effect on lead azide. Some results illustrating this are given in figure 5. It can be seen that in the absence of added water only very slight deterioration is suffered at temperatures of 80 ^{o}C or below; at 90 ^{o}C the reaction becomes detectable but is still almost insignificant under ambient humidity conditions. Other results in figure 5 show the slower attainment of equilibrium at 80 ^{o}C, 95 % RH, after a comparatively rapid loss of azide content during the first week, and demonstrate the dependence of the extent of hydrolysis on the size of the reaction vessel. The last two results in figure 5 show the substantial effects caused by introducing an alkaline absorbent for hydrazoic acid into the system, so preventing the attainment of equilibrium, or by introducing carbon dioxide.

Except for these last results, and bearing in mind the extreme severity of the test conditions the effects on the lead azide are in general quite small. This is in agreement with most past experience in which the most serious effect resulting from the hydrolysis has been not so much the extent of deterioration suffered by the azide as the extreme hazard caused by copper azide corrosion.

Reaction with Carbon Dioxide: Reaction with carbon dioxide often plays an important part in the deterioration of lead azide, and basic or, less frequently, normal lead carbonate is usually found as a decomposition product in systems where carbon dioxide is present.
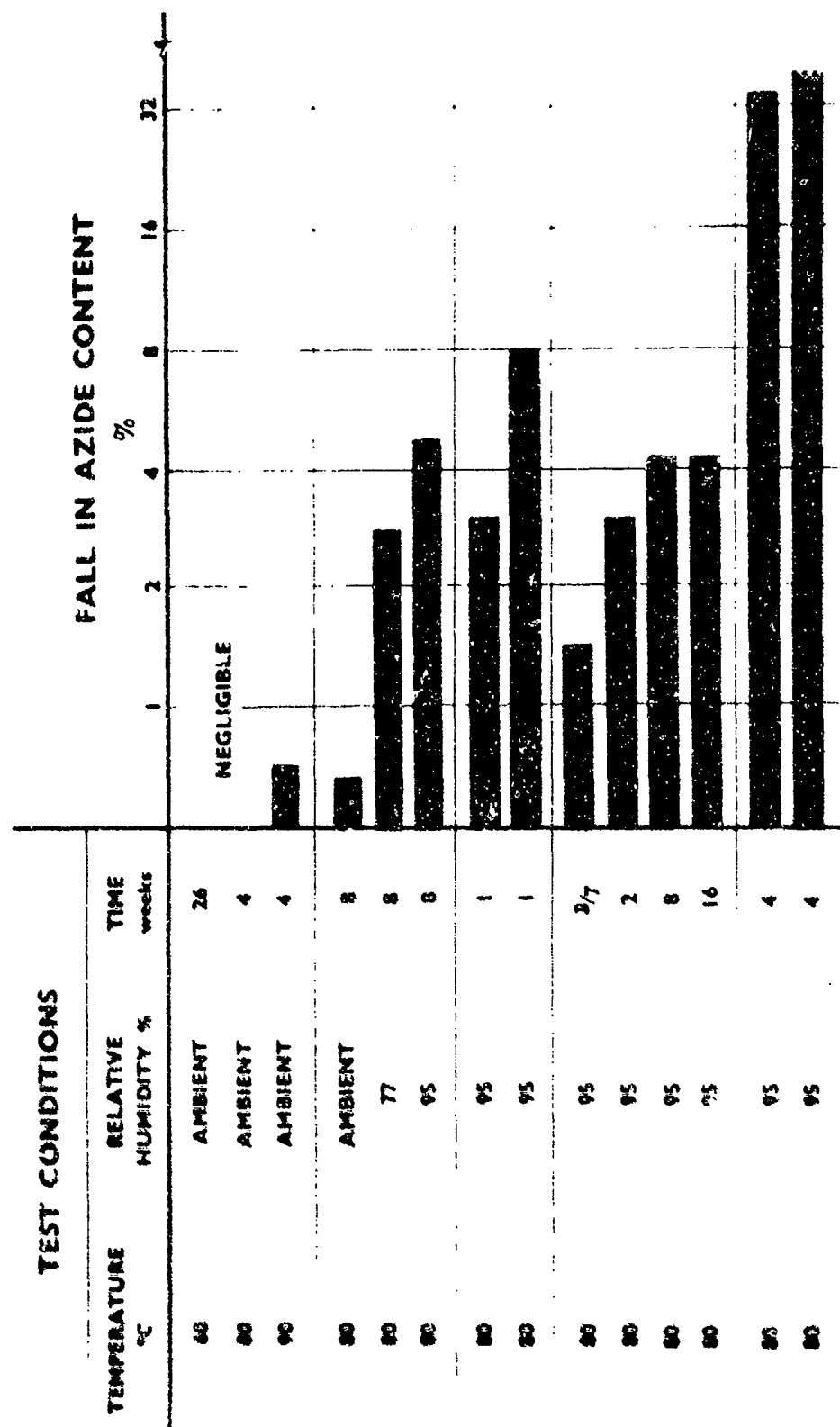
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TEST CONDITIONS

FALL IN AZIDE CONTENT %

| TEMPERATURE °C	RELATIVE HUMIDITY %	TIME weeks
40	AMBIENT	26
80	AMBIENT	4
90	AMBIENT	4
80	AMBIENT	8
80	77	8
80	95	8
80	95	1
80	95	1
80	95	3/7
80	95	2
80	95	8
80	95	16
80	95	4
80	95	4

NEGLIGIBLE

Figure 5. Effect of heat and moisture on lead azide

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Dry carbon dioxide is known not to react with lead azide and the effects of varying concentrations of water vapour on its reactivity have been studied qualitatively by an electron microscopic technique by Cook and al[3]. Their results showed that a slight reactivity was produced by introducing even fairly small amounts of water vapour, but that a high humidity was essential to obtain any substantial degree of reaction. Without added water only slight effects were produced even after 64 hours exposure at 100 °C. The work of Todd and coworkers[2] also led to a similar conclusion; storage in air containing 70 times the normal amount of carbon dioxide for 7 days at 60 °C, produced appreciable quantities of basic lead carbonate only as 100 % relative humidity.

There is no doubt however that carbon dioxide under moist conditions can greatly increase the extent of decomposition of lead azide and this is seen in figure 5 where a more than 10 fold increase in the loss of azide content was caused by introducing carbon dioxide.

Lamnevik considered the overall reaction with carbon oxide and water as:

$$3Pb(N_3)_2 \ (s) + 4H_2O \ (1) + 2CO_2 \ (g) \rightleftharpoons Pb_3(OH)_2(CO_3)_2 \ (s) + 6HN_3 \ (g) \qquad (ii)$$
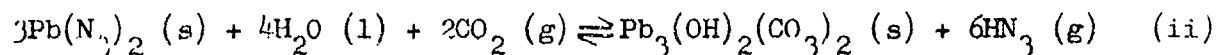
and derived the expression

$$K = p^6_{HN_3}/p^2_{CO_2}$$

for the equilibrium constant, indicating that the pressure of hydrazoic acid gas at equilibrium will be proportional to the cube root of the carbon dioxide concentration. The value of K was calculated as 8.7×10^{-11} at 25 °C. The validity of equation (ii) as representing the overall decomposition of lead azide is probably restricted by concentration, since at low concentrations of carbon dioxide the hydrolysis reaction (i) will predominate, and at high concentrations normal lead carbonate appears in the reaction products and the overall reaction will presumably be represented by:

$$Pb(N_3)_2 \ (s) + H_2O \ (1) + CO_2 \ (g) \rightleftharpoons PbCO_3 \ (s) + 2HN_3 \ (g) \qquad (iii)$$

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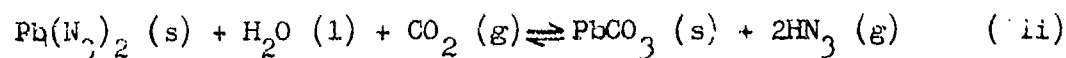
In this case the hydrazoic acid pressure would be proportional to the square root of the pressure of CO_2.

Effects of Physical and Chemical Environment: Since the reactions of lead azide with water or carbon dioxide are clearly reversible and governed by equilibria, the amount of deterioration of lead azide which occurs will in practice be influenced by a number of factors, including temperature, the partial pressure of reactants, the amount of lead azide which is involved, the volume of the container, and whether any leakage occurs from it.

It follows that if a substance capable of reacting with hydrazoic acid is placed in proximity to lead azide, then any hydrolysis which occurs is liable to be greatly increased. Such an effect has already been noted in figure 5 where lead azide was stored over an alkaline absorbent.

As well as this not unexpected reaction with an alkaline absorbent, hydrazoic acid is a labile compound reacting with metals, oxidizing and reducing agents, mineral acids, sulphides and sulphur, aldehydes, ketones and alcohols[4-6].

Its chemistry has been studied to only a limited extent and many other reactions probably await investigation.

In a weapon a relatively small lead azide specimen is normally part of an assembly containing much larger quantities of other material which may be either possible reactants for hydrazoic acid, or capable by their own slow deterioration of producing reactive substances e.g. carbon dioxide during storage in the system. They also, almost invariably, include items which are sources of enough water vapour to give a quite high humidity. As weapon designs and packaging become more elaborate, the variety of such materials and the likelihood of such incompatibility inevitably increases, and it becomes increasingly necessary to make appropriate tests to exclude undesirable materials or alternatively to have complete confidence in the protection given to the lead azide.

Method of Testing: The object of any test appropriate to the above situation must be to assess the effects of materials

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on the hydrolysis of lead azide. Only rarely will the material
being tested be intended for use in actual contact with the
explosive, and in most cases the quantities to be used will be
very much greater than the amounts of lead azide which will be
involved. An appropriate test therefore, is to store lead azide
under conditions which would normally produce a small but
detectable degree of hydrolysis, and to introduce into the
reaction vessel a relatively large amount of the material to be
tested. A compatible material will not cause an excessive
increase in the extent of the decomposition which is normally
obtained in its absence.

For reliable results to be obtained careful standardization
of the experimental conditions is necessary, to ensure that any
observed effects are caused by the material which has been
introduced and not by extraneous influences. A wide choice
exists for the conditions of such a test. The results in figure
6 were obtained by heating lead azide specimens weighing 0.05
grams for 4 weeks at 60 ^{o}C in small vacuum type desiccators,
capacity 500 ml. Each desiccator contained one azide specimen
in a small open beaker, with the material under test distributed
around it, and 10 grams of solid potassium sulphate moistened with
15 ml of saturated potassium sulphate solution to give a relative
humidity of 95 %. The desiccator lid was left with the tap open
and the assembly was placed in the 60 ^{o}C oven for two hours, to
allow for expansion of the enclosed air. The tap was then closed
and the heating continued for 4 weeks, after which time the
azide specimen was analysed for azide content using a gasometric
procedure similar to that of Blais[7] to measure the nitrogen
evolved by reaction with ceric ammonium nitrate.

Results of Compatibility Tests: The results in figure 6
show that the effect under these conditions can be considerable.
In the absence of sample materials the azide content (of British
Service Load Azide) falls by about 3 to 4 % in this test, but
many plastics and rubbers have been found which increase this
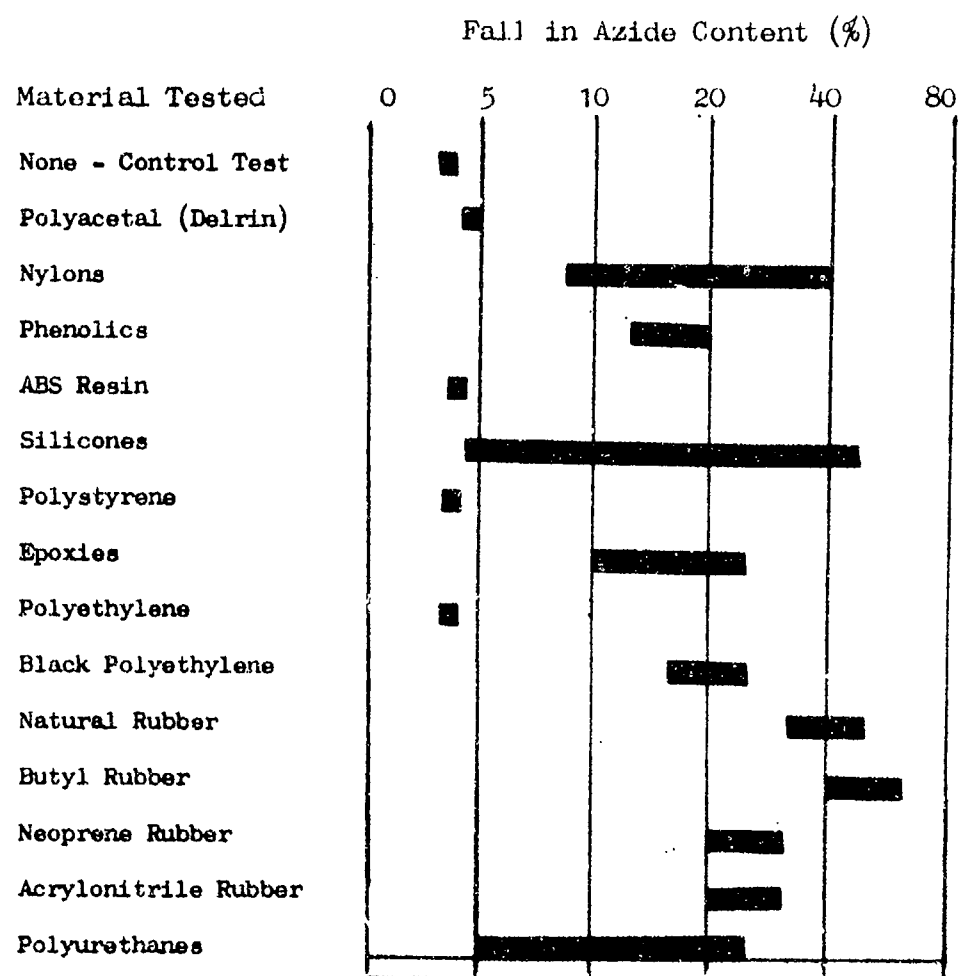degree of deterioration very markedly. Although these results

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Fall in Azide Content (%)

Material Tested	0	5	10	20	40	80

None - Control Test

Polyacetal (Delrin)

Nylons

Phenolics

ABS Resin

Silicones

Polystyrene

Epoxies

Polyethylene

Black Polyethylene

Natural Rubber

Butyl Rubber

Neoprene Rubber

Acrylonitrile Rubber

Polyurethanes

Figure 6. Proximity compatiblility tests. Lead azide 60 ^{o}C, 95 % R.H. 4 weeks

are quantitative chemical analyses for azide content, it would be wrong to regard the test as truly quantitative because of certain uncontrollable variables resulting from the differing properties of the materials under test. However, it does permit some discrimination between good and less good materials.

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